CEMENT AND LIME MANUFACTURE

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Continental Natural and Artificial Hydraulic Limes.

By DR. C. R. PLATZMANN.

LIME is obtained by burning limestone below the sintering temperature. In general we may distinguish three kinds of lime, namely: (1) quicklime, (2) weak hydraulic lime, and (3) strong hydraulic lime.

While quicklime hardens by the absorption of carbon dioxide from the atmosphere after being slaked, the term hydraulic lime is used to refer to materials produced by burning (also without sintering) limestones containing appreciable amounts of clay or magnesia to obtain a substance which will harden under water. The immediate cause of hardening in this case is not the absorption of carbon dioxide from the air but the formation of new compounds containing water of crystallisation. In burning after the expulsion of the CO_2 a reaction takes place between the solid phases—lime on the one hand and silica, clay, and iron oxide on the other—by which the percentage of substances soluble in hydrochloric acid is increased. This means that hydraulic limes are intermediate between quicklime and cement.

Hydraulic limes are successfully used under water, when the action of the water follows after a sufficient initial set in air. They are preferred for mortar used in masonry jointing and for rendering, when there are special requirements in respect of strength and weather resistance. The weak hydraulic limes are specially suitable for all kinds of masonry, where rapid setting and hardening of the mortar is desirable. For structures under water these limes are mixed with cement or pozzolanic materials such as trass or some kinds of slag, which increase their hydraulic and hardening properties. Weak hydraulic limes are also used in agriculture as fertilisers, in the manufacture of sand-lime bricks and for various technical purposes. Average tests of 1 : 3 hydraulic lime and sand mortars, stored for 72 hours in moist air and afterwards under water, show the following strengths:

						(lb. per square inch.)
Time (days)	.. ..	7	28	90	180	365
Tensile strength	.. ..	98	184	252	350	378
Compressive strength	..	378	456	1,316	1,764	2,141

The approximate compositions of limes and cements are shown in the following table :

TABLE I.

	CaO(MgO) after burning.	Clay content SiO_2, Al_2O_3, Fe_2O_3, etc.	Water content after slaking.
	per cent.	per cent.	per cent.
Quicklime	90—100	0—10	25—26
Weak hydraulic lime	85—90	10—15	20—24
Strong hydraulic lime	65—85	15—35	17—22
Roman cement*	55—60	40—45	—
Portland cement	60—66	34—40	—

There is great difference of opinion concerning the term hydraulic limes. As early as 1879 Hanenschild defined them as limes which are obtained from natural stones, which, after burning, slake to a powder with water and which harden under water after shorter or longer periods. Continental types of such limes are " Chaux du Teil " in France, the Beckum and Trier limes in Germany, and the lime of Prague in Czechoslovakia. In 1904 Schoch proposed that natural and artificial hydraulic limes should be classed as follows :

(I) Natural hydraulic limes :

(*a*) Real hydraulic limes containing over 70 per cent. of calcium carbonate.

(*b*) Roman cements containing 50 per cent. to 70 per cent. of calcium carbonate ; and

(*c*) Dolomitic limes.

(II) Artificial hydraulic limes :

(*a*) Lime with additions of natural materials (pozzolana, trass, etc.) ;

(*b*) Lime with additions of artificial materials (slag).

To distinguish weak and strong hydraulic limes one may accept the following definition.

Weak hydraulic limes are obtained from limestones by burning at less than the sintering temperature. They slake like quicklime, but do not swell quite so much. When left in a slaking pit they become hard after a time. The mortar obtained with these limes hardens in air by the absorption of carbonic acid and water, and after sufficient hardening in the air it continues to gain strength under water. These limes require a considerable time for hardening in air, never less than 7 days and at the most 21 days, before they may be exposed to the action of water. With hydraulic additions such as cement, trass, etc., they may be used under water earlier.

Strong hydraulic limes are products obtained by burning limestone below the sintering temperature. In dry slaking they crumble to powder, swell slightly, and develop heat. Their mortars harden in air and after sufficient air hardening, not exceeding 7 days, continue to harden under water.

* This term is incorrect ; it would be better to call it Roman lime.

It is apparent that conceptions of the term hydraulic lime vary to a large extent. We can, however, consider it a fact, that the only limes which can be designated as hydraulic are those which are produced by burning natural stone below the sintering temperature and to which no other ingredients have been added. Products, such as certain "extra-limes," not made from natural limestone or dolomite or to which other materials have been added either before or after burning cannot be designated as hydraulic limes. They represent mixtures for which a special classification would be appropriate.

For the manufacture of hydraulic limes the kilns are similar to those used for burning quicklime. The choice of the most suitable kilns for the purpose depends on the character of the raw material and fuel available, and the rate of production required. The occurrence of the raw material is in many varied forms. In one instance in Germany the limestone is found only 3 ft. below the surface of the ground. It is cut into cubes, stored for drying, burned for 24 hours and then ground. A Hessian hydraulic lime is burnt in an ordinary shaft kiln, using coke as fuel. Coal is generally used in the circular kiln. In the Rhineland a dolomitic limestone is burnt in a circular kiln at 1,800 deg. F. and is marketed in large pieces or as hydrated lime in bags. To produce 200 tons of lime, 396 tons of this dolomitic limestone are required. A certain clayey limestone in Silesia is quarried and broken to about 6-in. pieces and then calcined at 1,832 to 2,012 deg. F., and while still hot is sprayed with water. After cooling for two hours the lime is ground in a ball mill provided with screens and is then bagged. Separation of the ground lime is in most cases carried out by air separators. In Brunswick a marl is burnt at about 1,832 deg. F., slaked with water, and then left standing for six weeks. Before grinding in the ball mill 10 per cent. of well-slaked but under-burnt lime and 5 per cent. of cement clinker are added.

It is apparent from these different examples that the actual burning process offers no great technical difficulties. The kilns to be used are familiar types, and the slaking and grinding are relatively simple processes in which well-known machines are used.

The physical and chemical properties of hydraulic limes—that is, the calcined product—include the following:

(1) *Lime Content.* This is lower than that of quicklime, and varies between 65 per cent. and 85 per cent.

(2) *Loss on Ignition.* This amounts generally from 17 per cent. to 22 per cent.; it is lower than in quicklime but greater than in cement.

(3) *Colour.* The colour of slaked hydraulic lime depends on the raw material and differs greatly; while quicklime is generally white, hence the name "white lime."

(4) *Weight.* Hydraulic lime weighs considerably less than cement, but more than quicklime. The comparative weights are as follows:

	lb. per cubic foot.	
	Loosely filled.	Shaken.
Hydraulic lime	25 to 43·5	43·5 to 75
Quicklime	25 to 31	40 to 47
Portland cement	62 to 84	112 to 124

The specific gravity is similarly lower in quicklime than in Portland cement, and depends on the burning and slaking.

(5) *Strength.* The strength of hydraulic limes is higher than that of quicklimes but very much lower than that of Portland cement. All these properties are direct functions of the physical structure and manner of burning the raw material, and depend especially on the proportions of lime and clay. A definite lime content is essential in the stone, so that not all the lime shall be combined with the clay. For this reason it is doubtful whether the Roman cements, in which all the lime combines with clayey substances, may be rightly grouped with the hydraulic limes. The products marketed as cement lime are not different either in process of manufacture or in their properties from ordinary hydraulic lime. Besides these a number of limes are on sale which show extraordinary strengths approaching that of Portland cement, and which are invariably specially prepared or mixed products (" extra limes ").

Testing a hydraulic lime should comprise the following determinations :

(1) Slaking and yield ; (2) Weight (specific gravity as well as dry weight), loosely filled into container, shaken and tamped down ; (3) Screen analysis ; (4) Initial set ; (5) Soundness ; (6) Plasticity ; (7) Yield of mortar ; (8) Tensile and compressive strengths of mortar ; (9) Adhesion ; and (10) Chemical composition.

The percentages of the ingredients of hydraulic limes vary within the following limits :

	per cent.		per cent.
Silica	4 to 23	Magnesia..	0 to 6
Alumina..	1 to 15	Anhydrous sulphuric acid	0·1 to 3·5
Lime	60 to 88	Insoluble residue ..	0 to 7

It is apparent that even in this group of the true hydraulic limes great variations occur. Quite distinct from these are the dolomitic limes, which are low in calcium oxide but contain a considerable amount of magnesia and a smaller amount of silica. The composition may vary within the following limits :

	per cent.		per cent.
Silica	2 to 4	Magnesia..	11 to 39
Alumina and iron oxide	2 to 28	Anhydrous sulphuric acid	0·3 to 1·5
Lime	53 to 56	Insoluble residue ..	2·8 to 6

The writer is familiar with a large Rhenish works in which hydraulic lime is obtained from dolomite burnt at 1,832 to 2,192 deg. F. in a circular kiln, while stone from the same quarry is used in an adjacent plant for producing refractories by dead-burning at temperatures of 2,552 to 2,912 deg. F. His analyses of this dolomite give the following composition :

	per cent.		per cent.
Silica	0·84	Magnesia..	20·51
Alumina and iron oxide	1·88	Loss on ignition.. ..	45·00
Lime	31·67		
		Total ..	99·90

These figures for the uncalcined material may be compared with the figures previously given for the burnt lime.

Besides classifying hydraulic limes as weak and strong they may be arranged as follows: (1) Natural hydraulic limes (weak and strong); (2) Dolomitic limes; and (3) Special or "extra limes." The first two groups have already been discussed in detail. Some results with experiments on the third group will now be given, and it is intended to give further information in a later article. To show the great variation in composition and properties as well as the commercial designations, there are given with this a selection from the large number of specimens, tested by Burchartz at the Materials Testing Station (Berlin-Dahlen).

TABLE II.

COMPOSITION AND TENSILE STRENGTH OF VARIOUS LIMES.

	Loss on ignition.	SiO_2	R_2O_3	CaO	MgO	SO_3	Insoluble residue.	Alkaline residue.	28-day mortar strength (lb. per sq. in.)	
									Tensile.	Compressive.
Calcium limes.										
Black lime ..	17·21	16·66	9·45	65·01	1·47	0·74	7·02	—	—	—
Hydraulic lime..	21·04	20·35	8·35	67·45	1·32	0·68	—	1·85	37	114
Cement lime ..	16·32	12·31	7·85	68·58	0·71	3·29	6·56	0·70	70	242
Lean lime ..	14·98	15·71	2·58	75·76	—	0·40	5·47	—	86	312
Cement lime ..	4·87	10·73	4·04	81·81	0·84	1·40	—	—	65	341
Marl lime ..	5·66	3·94	3·60	86·28	0·76	2·26	2·88	0·28	4(!)	13(!)
Grey lime ..	24·16	6·17	3·23	88·98	0·90	0·13	—	0·59	34	42
Dolomitic limes.										
Black lime ..	20·08	4·07	5·82	54·69	33·75	0·45	—	—	63	185
Cement lime ..	1·85	3·32	2·20	55·40	38·79	—	—	—	29	70
Hydraulic lime..	18·68	2·40	7·43	56·33	33·71	0·32	—	—	74	155
Special limes.										
A	16·32	24·07	6·33	57·10	0·22	1·00	9·63	1·65	380	1,920
D } From same	9·27	24·01	6·01	59·59	0·22	0·99	7·54	1·65	550	4,300
G } plant	9·55	29·28	2·65	61·25	1·04	1·16	1·42	0·20	550	5,900

The writer's investigations on various samples gave the following results. A sample designated "Red Lime" from Degerhamm (Sweden) showed the following composition:

	per cent.		per cent.
Silica	24·05	Sulphide	0·47
Alumina and iron oxide	14·59	Anhydrous sulphuric acid	3·90
Lime	41·80	Loss on ignition.. ..	13·46
Magnesia	1·03		
		Total	99·30

With this material the following strengths were obtained. In a 1 : 3 mixture with sand at 56 days, 650 lb. per square inch in compression. A mixture of 15 per cent. of "Red Lime" and 25 per cent. of siliceous material mixed with standard sand, 1 : 3, gave an average compression strength of 1,460 lb. per square

inch at 28 days and 2,071 lb. per square inch at 56 days. The siliceous material used was rich in silica, soluble in hydrochloric acid, which enabled it to combine with the lime to form silicates.

Analysis of a strong hydraulic lime from Thuringia resulted as follows :

	per cent.		per cent.
Silica	23·10	Sulphide	0·44
Alumina and iron oxide	13·40	Anhydrous sulphuric acid	0·63
Lime	51·92	Loss on ignition.. ..	8·28
Magnesia	1·92		
		Total	99·69

The compressive strength of a 1 : 3 mixture with standard sand was 770 lb. per square inch in 7 days and 1,135 lb. per square inch in 28 days. With an admixture of 25 per cent. of siliceous material the compressive strength was 1,890 lb. per square inch in 7 days and 2,430 lb. per square inch in 28 days.

It is apparent from the different investigations, that there is no direct relation between the chemical compositions and the hardening properties of the different types of hydraulic lime, and that the lime content is not a reliable criterion of the attainable strength. The varying physical properties of the raw material, such as density and crystalline structure, do not explain differences in hardening. The variations in properties are rather due to the burning process, which in its turn is partly influenced by the physical properties. The hardening properties of a lime will increase or diminish according to how (after the expulsion of the carbon dioxide) the process of forming silicates is carried on, that is the reaction between the solid substances, lime on the one hand and silica, alumina and iron oxide on the other hand.

Magnesian Hydrated Lime.

The Breedon and Cloud Hill Lime Works, Ltd., of Isley Walton, Derbyshire write :—

We read with interest your reference to the use of magnesian hydrated lime, and also your reader's contribution with regard to the use of this material in South America. We market a high magnesian hydrated lime which is being used successfully in the building, plastering, and chemical trades. The chemical analysis is as follows :—

	Per cent.
Silica	1·39
Iron oxide and alumina	2·65
Calcium oxide	42·98
Magnesia	34·60
Loss (water of hydration)	18·38

The Cooling of Rotary Clinker—III.

By W. GILBERT, Wh. Sc., M.Inst.C.E.

(51) The earlier articles in this journal (July and October, 1937) described some small-scale experiments on the cooling of spherical lumps of rotary clinker in an air stream originally at 60 deg. Fah. The formula representing the experimental results was

$$H_c = \frac{0.328\ Wa^{0.5}}{D^{0.35}} \qquad \ldots \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (5)$$

The meaning of the symbols is given in para. (50).

(52) In deriving the formula it was necessary to assume that the surface temperature and the rate of heat transfer would be at any instant uniform over the surface of the spherical lump during the cooling process. An experiment is, however, cited by McAdams (see "Heat Transmission," 1933 ed., p. 215) in which air was flowing at right-angles to the axis of a cylinder. The rate of

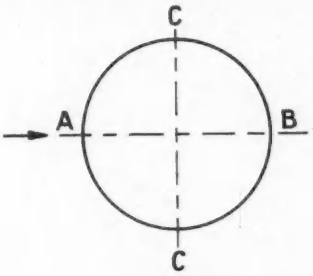

Fig. 14.

heat transfer was found to be equal at the front and back (see points A and B on *Fig.* 14) ; at the sides (C), however, it was only 40 per cent. of that at A and B. It will be seen, therefore, that during cooling the rate of heat transfer, and the surface temperature, may not be uniform over the surface of a spherical lump, but formula (5) will give an average value for H_c which can be applied in practice.

(53) VARIATION OF H_c WITH TEMPERATURE DIFFERENCE.—When working out the experimental results each cooling curve was divided into periods as shown in Table VII (October, 1937) and the average value of H_c for each short period was calculated. It was found, generally, that after cooling by radiation had been allowed for the value of H_c for the early periods, where the temperature difference was greatest, might be as much as 50 per cent. more than the value of H_c near the end of the curve, where the temperature difference was least.

Relation between the Nominal and the Actual Value of H_c.

(54) The values of H_c which are given by formula (5) are based on the assumption that the whole of the air (at a temperature of 60 deg. Fah.) which approached the grid was uniformly heated by the cooling clinker, and, since the air was in

excess, its calculated temperature rise was only a few degrees. Hence the temperature difference assumed to be available for cooling at any instant was substantially the surface temperature of the clinker less 60 deg. Values of H_c so determined can conveniently be applied in practice.

(55) It can be shown, however, that the temperature of the air adjacent to the clinker lump must rise with extreme rapidity whilst the outlying portions of the stream are not affected. Hence the temperature difference between the clinker surface and the adjacent air will be much less than that estimated in accordance with para. (54), and consequently the actual value of H_c will in all cases be greater than the nominal value given by formula (5).

The real value of H_c, which is based on the rate of heat transfer, and on the difference between the surface temperature of the clinker and the surface temperature of the air adjacent, is denoted by HH_c. It is possible that HH_c may be approximately constant for air and rotary clinker.

(56) Particulars which relate to the probable value of HH_c are gathered together in Table IX.

TABLE IX.—PARTICULARS RELATING TO THE VALUE OF *HHc* FOR AIR AND CLINKER.

Line No.	Grade.	Lump diameter D (inches).	Air velocity, feet per minute at 60 deg. Fahr.	Time of contact, air and clinker. Unit $\frac{1}{1000}$ second.	Values of *Hc*.			Maximum thickness of hot air layer (inches).
					By formula (5)	*HHc* 200, K 0.0133	*HHc* 200, K 0.030	
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
1	23 grn.	1.05	1,373	3.82	25.7	15.4	22.4	0.059
2	do.	1.02	573	8.90	16.6	10.8	15.6	0.078
3	do.	1.03	163	31.60	8.9	5.8	8.2	0.156
4	V	0.34	1,482	1.15	39.5	26.5	37.4	0.033
5	do.	0.34	618	2.75	25.5	17.9	25.6	0.046
6	do.	0.33	176	9.38	13.6	10.6	15.2	0.078
7	VII	0.15	1,745	0.43	56.9	41.8	55.6	0.013
8	do.	0.15	728	1.03	36.8	27.8	39.0	0.026
9	do.	0.15	207	3.62	19.6	15.8	23.0	0.052
10	Beyond experimental range	5.00	1,200	20.83	13.8	7.2	10.2	0.118
11		0.01	1,200	0.042	121.8	97.4	116.6	0.005

Cols. (1), (2), (3), and (5) are reproduced from cols. (1), (2), (3), and (9) of Table VIII (October, 1937), but some of the grades are omitted. Col. (4) gives in each instance the time required for an air particle to travel a distance equal to the lump diameter at the velocity given in col. (3); this is taken to be approximately the time of contact. The unit of time is one-thousandth of a second.

Lines (10) and (11) give by way of example two diameters, one well above and one much below the experimental range. The air velocity assumed is 1,200 ft. per minute.

(57) The rise of the air surface temperature during contact with the clinker, for various lump diameters and air velocities, may be approximately estimated in the first instance by assuming that the air moves smoothly over the surface of the lump, so that heat is transmitted across the stream at right angles to the direction of flow by conduction only.

Referring to *Fig.* 15, ABC represents a column of air which may be 1ft. square in cross section. The surface AB receives heat from a hot body *D*, by convection, and the value of HH_c is assumed to be 200. The temperature of the hot body D, which is constant, is taken at 100, and the initial air temperature at 0. The conductivity K for air at 60 deg. Fah., when expressed in B.T.U. per square foot per hour per deg. Fah. per foot thick, is 0.0133. (The conductivity of rotary clinker is about 31 times that of air.)

(58) The temperature rise of the surface AB after any period of heating can be obtained by Schmidt's method, as described in this journal for February, 1936, pages 27 and 28. Referring to formula (15), there given, gT will now represent the temperature of the hot body, which is 100. (Owing to a clerical error the denominator was wrongly given; it should read $3K + Hx$, not $3K - Hx$.)

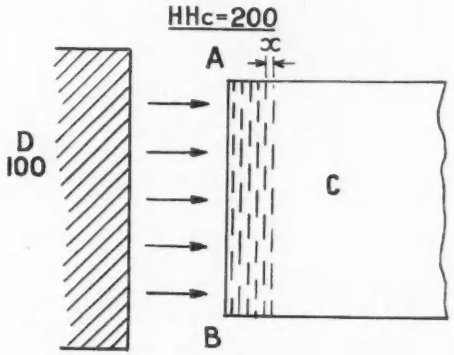

Fig. 15.

In formula (14), the air density W at 60 deg. Fah. is taken at 0.0763, and the air specific heat ϕ, at 0.24.

(59) In this formula the pound, foot, and hour system is used. The calculation is divided into four stages, the values of t (the length of each elementary heating period) being 1, 9, 81, and 729×10^{-9} hours respectively. The corresponding values of x, the width of each elementary plate in feet, will be 0.0000382, 0.000115, 0.000343, and 0.00103.

Taking the first stage of the calculation, for a period $t = 1 \times 10^{-9}$ hours and $HH_c = 200$, formula (15) becomes

$$aT = 32.1 + \frac{L}{8.35} + \frac{M + R}{3.57}$$

When t changes to 9×10^{-9} hours the width of each elementary plate x is multiplied by 3, so that a new line of temperatures is easily obtained.

(60) The result of the earlier part of the calculation is shown by the graph in *Fig.* 16. In order that time may be better appreciated, the unit used for the base

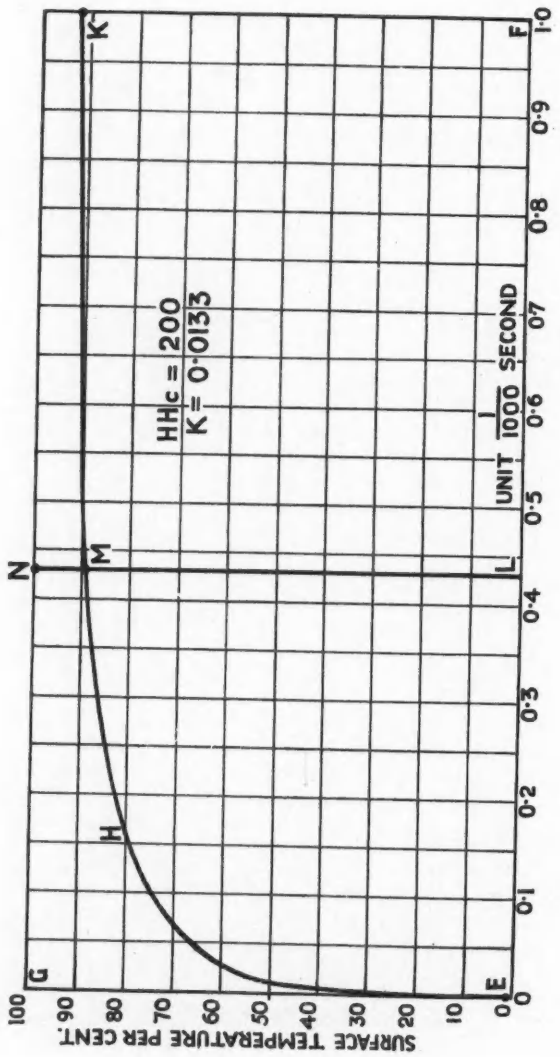
SURFACE TEMPERATURE PER CENT.
100
90
80
70
60
50
40
30
20
10
0
G
H
N
M
L
K
E
F
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
1·0
UNIT 1/1000 SECOND
HHc = 200
K = 0·0133

Fig. 16.

line is $\frac{1}{1000}$ second. Hence the distance EF represents one-thousandth of a second, or 277×10^{-9} hours. The temperature rise of the surface AB in *Fig.* 15 during the first one-thousandth of a second is shown by the curve EHMK.

(61) On referring to Table IX it will be seen, for instance, from line (7), that the air will pass a lump of grade VII clinker in $\frac{0.43}{1000}$ second. This period falls within the scope of the graph, and the end of the period is denoted by the ordinate LMN. EG represents the initial temperature difference between the air and the clinker, which was taken at 100. At the end of the period EL the available temperature difference has been reduced to MN, which is only 11 per cent. of EG. The mean temperature difference over the period EL, as measured from the graph, is found to be 20.9 per cent. of EG, and this is a measure of the heat transmitted.

The value of HH_c assumed in this instance is 200, but the value of H_c over the period EL, when estimated on the full temperature difference EG as it was in the clinker cooling experiments, would only be $\frac{200 \times 20{\cdot}9}{100}$, or 41·8. This quantity is entered in col. (6). The value of H_c, by formula (5), see line (7), col. (5), was 56·9.

(62) Again taking line (3) of Table IX, where the lump diameter is larger and the velocity less, the time of contact is now $\frac{31{\cdot}6}{1{,}000}$ second, and an extension of the graph in *Fig.* 16 shows that the mean temperature difference for the period is only 2·9 per cent. of EG, leading to a value of H_c of 5·8. The value of H_c by formula (5) is 8·9.

Proceeding in this manner the remaining figures in col. (6) are obtained, and it will be seen by comparing cols. (5) and (6) that, if the heat from the cooling clinker is distributed across the air stream by conduction only, a value of $HH_c = 200$ would not cool the clinker as quickly as it was cooled in practice.

(63) It is found on trial that an increase in the value of HH_c to 400 would also not be sufficient, since the curve EHMK in *Fig.* 16 rises more quickly, and the available temperature difference is correspondingly reduced. It may be pointed out that the value of the initial temperature difference, EG in *Fig.* 16, is not material, since for any value of EG the curve EHMK will give the temperature rise per cent.

(64) It is generally assumed in similar problems that part of the heat is transferred across the air column during cooling by a movement of the air at right-angles to the direction of flow. This movement may be approximately allowed for by increasing the value of K, in this instance from 0·0133 to 0·030, if HH_c is taken at 200 as before.

The temperature rise of the air surface AB in *Fig.* 15 has been again calculated, using the revised value for K, and the figures in Table IX, col. (7), show the values found for H_c. The agreement between cols. (5) and (7) is seen to be

quite good, even for lump diameters far beyond the experimental range as shown in lines (10) and (11).

(65) The values of H_c listed in cols. (6) and (7) of Table IX have been obtained by the aid of assumptions which are only partly true. It is, however, clear that the rapid cooling of rotary clinker is prevented by the almost instantaneous rise of the air surface temperature to that of the clinker surface temperature very nearly. It will also be seen from cols. (6) and (7) that the use of a constant value for HH_c, when the time of contact is taken into account, leads approximately to the same variation in the value of H_c as is caused in practice by changes in the lump diameter and in the air velocity. Further investigation is, however, desirable.

(66) Col. (8) in Table IX shows how far the temperature rise penetrates into the air stream during contact. It is seen to be quite small. These distances were obtained when the air temperature rise was worked out by Schmidt's rule in order to obtain the figures in col. (7). For instance [see line (1)], a lump 1 in. in diameter was cooled in an air stream 3 in. square which moved at a velocity of 1,373 ft. per minute, but the cooling was done by an air layer not more than $\frac{1}{17}$ in. thick. Apparently when air passes a hot clinker lump a very thin, highly heated layer is produced, which later mixes with the general stream.

(To be continued.)

The Thermal Efficiency of the Rotary Cement Kiln.*

By HANS GYGI (ZURICH).

(Continued.)

IV—HEAT TRANSFER.

(1) Heat Transfer Distribution along the Axis of the Kiln per m.² of the Inner Surface of the Lining.

FOR the purpose of calculating the gas temperatures we have already determined the quantity of heat required to raise the temperature of the raw material by a given amount. If, for any part of the kiln, we add to this quantity of heat the amount lost by radiation from the outside of the kiln and divide the sum by the area of the inner surface of the 200-mm. lining in the part of the kiln under consideration we obtain a curve which represents the heat transfer distribution along the kiln axis in Kcal./m.²h. The shape of the curve (*Fig.* 15) is of the utmost

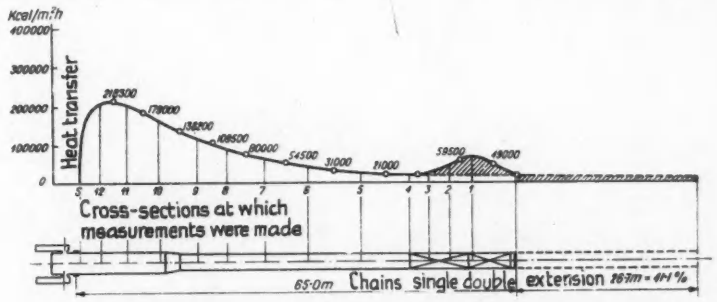

Fig. 21.—Determination of the length of a kiln without chains in which, other things being equal, the exit temperature of the gases would be the same as in the existing shorter kiln with chains.

practical importance, and in the following paragraphs detailed consideration will be given in turn to the values for the drying zone, the pre-heating zone, and the burning zone, all of which are based upon experimental results.

(2) Heat Transfer in the Drying Zone.

Unfortunately it is impossible to calculate the heat transfer for the various cross sections in the drying zone from the measured temperatures. This part of the kiln is fitted with chains and it would be necessary, for the purpose of the calculation, to know the temperatures on the surfaces of the links of the chains; but these cannot be measured. Even if they could, the calculation would still be impossible, since heat transfer coefficients have yet to be determined for the

* Continued from "Cement and Lime Manufacture," November and December, 1937, and February and March, 1938.

case of a curtain of chains at right angles to a stream of gas. We must therefore restrict ourselves to a consideration of the principles underlying the transfer of heat in the drying zone. This seems all the more justifiable when it is remembered that the function of the chains is not only to intensify heat transfer but also to break up any lumps of slurry that may be formed.

It will be seen from *Fig.* 21 that heat transfer decreases steadily from the burning zone to the drying zone because radiation from the gases decreases as the temperature falls. It is therefore natural that for many years endeavours have been made to improve the heat transfer by convection in the drying zone by means of the most various devices. It is remarkable that, of all these appliances, chains have proved the most suitable ; more massive fittings have always been more or less destroyed after comparatively short service.

The utility of the chains has been shown in *Fig.* 21, in which, by means of the extrapolated heat-transfer curve, an estimate has been made of the length of kiln required if chains were not fitted. It has been assumed that working conditions and the exit gas temperature would be the same in the longer kiln without chains as in the shorter kiln with chains. It will be seen that it would be necessary to increase the length of the kiln by 26,700 mm.

The *modus operandi* of the chain system is that during the slow rotation of the kiln one part of the chains is exposed to the hot gases while the other part is immersed in the slurry. Near the slurry inlet the chains in the gas stream are also covered with slurry, but these are not heated appreciably and merely serve to increase the surface of slurry exposed to the gases. On the other hand, the action of the chains is quite different in that part of the drying zone where the raw material has been dried to such an extent that it no longer adheres to them. Here the chains take up heat as long as they are exposed to the gases and give it up again to the raw material in which they are subsequently immersed. Chains promote heat transfer in the slurry zone by increasing the surface of the slurry in contact with the hot gases, while in the zone where the material is earth moist their action is of the regenerative type. It will be seen from *Figs.* 8 and 15 that heat transfer shows a distinct maximum at the cross section where the slurry is transformed from the liquid to the earth-moist state. It is not possible to use chains in that part of the kiln where the raw material is quite dry, because the exit gas would then carry off too much dust. Practical experience has shown that the raw material should have a residual moisture content of 5 to 10 per cent. when it leaves the zone fitted with chains. This has the further advantage that at the hot end of the zone ordinary mild steel chains are able to withstand the temperature, and it is not necessary to go to the expense of fitting chains of special steel.

After these preliminary remarks we may consider, on the basis of the coefficients for the heat transfer by convection from combustion gases to the tubes of a water-tube boiler, the best arrangement of chains for the promotion of heat transfer in the rotary kiln. In his book on water-tube boilers Münzinger[18] used the values determined experimentally by Reiher to prepare a most instructive

series of diagrams showing the heat transfer from gas to tubes as influenced by gas temperature, tube temperature, length of tube, gas composition and velocity, and the diameter of the tube. He studied the cases of gas flow normal to and parallel to the tubes and, for the case of flow at right angles, both a staggered and a straight-line arrangement of the tubes.

The values given in *Table* 12 are obtained from Münzinger's diagrams for the three arrangements of the tubes and for a gas temperature of 1,030 deg. C., a tube temperature of 265 deg. C., a gas velocity of 6 metres per second, an overall diameter of tube of 83 mm., with ten rows of tubes, and using bituminous coal as fuel.

TABLE 12.—HEAT TRANSFER COEFFICIENTS FOR VARIOUS ARRANGEMENTS OF BOILER TUBES.

Flow normal to tubes.		Flow parallel to tubes. (Kcal./m.² h deg. C.).
Staggered (Kcal./m.² h deg. C.).	Straight line (Kcal /m.² h deg. C.).	
31·5	22·6	12

These values would be higher for smaller tube diameters.

It is clear that with chains in the kiln the gas flow and the arrangement exert a similar effect to that in the water-tube boiler. Furthermore, the comparison shows that it is possible to find the efficiency of chains by simple calculations.

(3) Heat Transfer in the Pre-heating Zone.

Although it is not possible to calculate the heat transfer in the drying zone, which is fitted with chains, from the temperatures measured in the experiments, this can be done for the pre-heating zone. In the following paragraphs the calculation will be made for cross section C.

(1) CALCULATION OF THE HEAT TRANSFER FROM THE GASES FOR 1 m. LENGTH OF KILN.—Heat is given up by the gases to the wall of the kiln and to the raw material by radiation and convection. The process may therefore be expressed by

$$Q_{Gas} = Q_{Radiation\ G.W.} + Q_{Radiation\ G.M.} + Q_{Convection\ G.W.} + Q_{Convection\ G.M.} \qquad (12)$$

The radiation from the gas is calculated by the approximate formulæ derived by A. Schack[19] which allow the radiation from the carbon dioxide and the water vapour in the gases to be taken into account. These formulæ are based on measurements of the three bands in the spectrum in which carbon dioxide and water vapour absorb radiation and on the absorption coefficients of the two gases for the different wavelengths. In the case of radiation from a gas, Kirchhoff's law is not sufficient for the determination of the relation between the absorption of radiation passing through the gas and the radiation emission of the gas itself. Nevertheless, Schack succeeded in finding this relation by investigating the temperature equilibrium within a hollow body of the shape of the gas volume from which the radiation is emitted.

The equation for the radiation from the carbon dioxide is

$$q_{co_2} = \frac{C}{4{\cdot}95}\left[\phi_1(K_1 - K'_1)\left(1 - \frac{1 - e^{-16c}}{16c}\right) + K_2 - K'_2 + \phi_3(K_3 - K'_3)\left(1 - \frac{1 - e^{-80c}}{80_e}\right)\right] \text{Kcal./m.}^2\text{h.} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (13)$$

where

q_{co_2} = the quantity of heat transferred by radiation from the carbon dioxide (Kcal. per sq. m. per hour) ;

c = an abbreviation for the term p × s ;

p = the partial vapour pressure of the carbon dioxide ;

s = the thickness (m.) of the radiating layer over the irradiated surface ;

e = base of Napierian logarithms ;

K = the radiation of the individual absorption layers of an infinitely thick layer of carbon dioxide in Kcal. per sq. m. per hour ; K at the temperature of the gases, K′ at that of the irradiated surface ;

C = the radiation coefficient of the irradiated surface ;

ϕ = correction factors to make the results obtained by means of the approximate formulæ agree with those given by the exact expression, which is not cited here. They depend upon the value of c and the shape of the radiating gas volume. For the conditions under consideration, ϕ may be taken as unity.

The expression for the radiation emitted by the water vapour is

$$q_{H_2O} = \frac{C}{4{\cdot}95}\left\{\phi_1(w_1 - w'_1)\left(1 - \frac{1 - e^{-8e}}{8e}\right) + \phi_2(w_2 - w'_2)\left[1 - \frac{0{\cdot}66}{5e}(1 - e^{-5e}) - \frac{0{\cdot}34}{22c}(e^{-5c} - e^{-27c})\right] + \phi_3(w_3 - w'_3)\left(1 - \frac{1 - e^{-45c}}{45c}\right)\right\} \text{Kcal. per sq. m. per hour} \quad .. \quad .. \quad .. \quad (14)$$

where w = the radiation of the individual absorption layers of an infinitely thick layer of water vapour in Kcal. per sq. m. per hour, and

ϕ = factors as in (13).

The values for K and W were taken from tables 19 and 20 in A. Schack's work on industrial heat transfer[20].

Having shown how the radiation from the gases can be calculated, we proceed to determine the quantity of heat transferred by convection. The best expression for heat transfer by convection for the case of forced turbulent flow in tubes is that given by W. Nusselt, viz.,

$$\alpha = 0{\cdot}2521\frac{\lambda_{wall}}{d^{0.214}}\left(\frac{wc_p}{\lambda}\right)^{0.786} \text{Kcal. per sq. m. per hour per deg. C.} \quad .. \quad (15)$$

in which

λ_{wall} (Kcal./m.h. deg. C.) = the thermal conductivity of the gas at the temperature of the tube wall ;

λ(Kcal./m.h. deg. C.) = the thermal conductivity of the gas at its mean temperature ;

C_p(Kcal./m³. deg. C.) = the specific heat of the gas at working temperature per m.³ ;

$w\left(\frac{\text{m.}}{\text{h.}}\right)$ = the velocity of the gas under working conditions; and

d(m.) = the internal diameter of the tube.

Nusselt found later that it is better to substitute λ for λ_{wall}. Adopting the slightly different form of W. Nusselt's equation used by H. Groeber[21], and substituting the constant 0·0285 for the constant 0.2521 to bring the expression into agreement with the experimental results, we have

$$\alpha = 0{\cdot}0285 \frac{W_0^{0.786} \times C_p^{0.786} \times \lambda^{0.214}}{d^{0.214}} \text{ Kcal./m}^2\text{.h. deg. C.} \quad .. \quad .. \quad (16)$$

which enables us to calculate the heat transferred by convection. After these general remarks we are in a position to undertake the addition of the various terms in equation (12).

The temperatures of the gases, the lining, and the material at cross section 6 are :

Mean gas temperature	t_g	= 1,218 deg. C.
Mean temperature of exposed lining	t_w	= 720 deg. C.
Temperature of material	t_m	= 500 deg. C.

The products of the partial pressures of the carbon dioxide and the water vapour multiplied by the thickness of the layer are

$$C_{CO_2} = 0{\cdot}44$$
$$C_{H_2O} = 0{\cdot}10$$

$Q_{\text{Radiation G.W}}$

$$q_{CO_2} = 14{,}000 \text{ Kcal./m}^2\text{.h.}$$
$$q_{H_2O} = 22{,}500 \text{ Kcal./m}^2\text{.h.}$$
$$q_{G.W.} = 36{,}500 \text{ Kcal./m}^2\text{.h.}$$
$$Q_{G.W.} = q_{G.W.} \times F_w \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (17)$$

in which

F_w = the surface of exposed lining per metre length of kiln

from which

$$Q_{\text{Radiation G.W.}} = 161{,}000 \text{ Kcal.m.h.}$$

$Q_{\text{Radiation G.M.}}$

$$q_{CO_2} = 17{,}700 \text{ Kcal./m}^2\text{.h.}$$
$$q_{H_2O} = 27{,}000 \text{ Kcal./m}^2\text{.h.}$$
$$q_{G.M.} = 44{,}700 \text{ Kcal./m}^2\text{.h.}$$
$$Q_{G.M.} = q_{G.M.} \times F_m \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (18)$$

in which

F_m = the surface of the material per metre length of kiln.

from which

$$Q_{\text{Radiation G.M}} = 98{,}300 \text{ Kcal./m.h.}$$

$Q_{\text{Convection G.W.}}$

$$q_{G.W.} = \alpha(t_g - t_w) \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (19)$$

in which, according to equation (16),

$$\alpha = 6{\cdot}54 \text{ Kcal./m}^2\text{.h. deg. C.}$$
$$Q_{G.W.} = \alpha(t_g - t_w)F_w \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (20)$$

and $Q_{\text{Convection G.W.}} = 14{,}300$ Kcal./m.h.

$Q_{\text{Convection G.M.}}$

$$q_{G.M.} = \alpha(t_g - t_m) \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (21)$$
$$Q_{G.M.} = \alpha(t_g - t_m)F_m \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (22)$$

and $Q_{\text{Convection G.M.}} = 10{,}300$ Kcal./m.h.

Therefore we have for the total heat transfer from the gases for 1 m. of length of kiln :

	Kcal./m.h.
$Q_{\text{Radiation G.W.}}$	= 161,000
$Q_{\text{Radiation G.M.}}$	= 98,300
$Q_{\text{Convection G.W.}}$	= 14,300
$Q_{\text{Convection G.M.}}$	= 10,300
$Q_{\text{Gas calculated}}$	= 283,900 Kcal./m.h.

The heat transfer determined experimentally for the cross section under consideration was

286,000 Kcal./m.h.

so that the agreement with the measured values is very good.

A similar calculation of the heat transfer from the gases at cross section 5 gave a higher value than the experiment, whereas for cross section 8 the calculated value was lower. The reason for the discrepancies in the cooler cross sections is probably that the absorption coefficients from which the values for the radiation from water vapour (w) in Schack's equation are derived are too low. For the hotter cross sections, the differences are probably due to the fact that no allowance has been made for the radiation from the dust particles which becomes increasingly significant as the flame is approached.

(To be continued.)

Institution of Works Managers.

An Institution of Works Managers is being formed with the object of raising the status and prestige of works managers. It is proposed that the headquarters of the institution shall be in Manchester. The acting secretary is Mr. L. M. Angus-Butterworth, of Ashton New Hall, Ashton-on-Mersey, Cheshire, from whom further details may be obtained.

SUPER REFRACTORIES for CEMENT KILNS

ALITE No. 1. 68% ALUMINA
Refractory Standard 3260° Fahr.
ALITE B. 57% ALUMINA
Refractory Standard 3180° Fahr.
ALITE D. 41% ALUMINA
Refractory Standard 3150° Fahr.

E. J. & J. PEARSON, LTD.,
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The Estimation of Free Lime in Portland Cement.

A useful résumé of methods of estimating the free lime in Portland cement is given in *Tonindustrie Zeitung* (1936, p. 1021). It is pointed out that in 1933 P. Schläpfer and R. Bukowski published a paper on "A Method for the Estimation of Free Lime and Calcium Hydroxide in Cements and Cement Clinkers."[1] This method has been widely used and is known as the "Glycolate" method. The authors use ethylene glycol instead of glycerine[2] as the solvent for free lime because the latter has a number of disadvantages although it gives satisfactory analytical results. It has been shown that an efficient wetting and thorough dispersion of the cement is essential for the rapid and accurate determination of free lime or calcium hydroxide. This is not very easy to accomplish with glycerine alone, and, therefore, in the "Glycerate" method some ethyl alcohol is added. The addition of alcohol, however, tends to retard the formation of the glycerate, and a search was therefore made for another reagent which did not have this disadvantage. Ethylene glycol is such a reagent and has good wetting properties, besides being capable of forming an alcoholate with calcium oxide and calcium hydroxide. In this method the ground material together with a pinch of quartz granules is mixed with ethylene glycol and shaken in a water bath for half an hour at 65 to 70 deg. C. In the case of light coloured materials the mixture is titrated with N/10 benzoic acid, using phenolphthalein-α-naphtholphthalein as indicator, the end point being indicated by a rose-brown coloration of the liquid. Usually the mixture is filtered before titration. In this case N/10 hydrochloric acid is used for titrating with the same indicator or with methyl orange.

The work on which this method is based, together with further results, was published by P. Schläpfer and P. Esenwein[3] a short time ago. This paper is divided into three sections. The first deals with Bessey's method of estimating calcium hydroxide in hydraulic cements, the second describes a microchemical method of determining calcium oxide, and the third describes a method of analysis for estimating free lime by the "glycolate" or modified glycerate method.

The first and second sections deal with the very important question of the determination of calcium oxide and calcium hydroxide which is useful for material which is not quite fresh, for instance, clinker or cement which has taken up moisture, or even set cement. For this type of material Bessey's method has been recommended. It is based on the assumption that the hydrated compounds in cement, with the exception of calcium hydroxide, lose their water content below 350 deg. C., while calcium hydroxide is dehydrated between 350 and 550 deg. C. Schläpfer has found that this method gives too high a result for free calcium hydroxide and has shown that not only the calcium hydroxide but also the hydrated calcium silicates and aluminates retain a considerable portion of their combined water when heated at 350 deg. C. for several hours.

Schläpfer and Esenwein have worked out a microchemical method for distinguishing free lime and calcium hydroxide which, though it does not give a

quantitative separation, allows a good idea of the proportions to be obtained. An accidental observation acted as a basis for these investigations, which was then systematically followed up. In the microscopical investigation of synthetic cement constituents it was found that natural clove oil which was used as the immersion fluid reacted with the calcium oxide present. Immediately after the addition of clove oil a strong yellow colour developed around the individual CaO particles and the refractive index of this coloured zone increased. After about ten minutes a new substance began to crystallise out at the periphery of the lime particles ; the crystals grew rapidly and showed a strong birefringence. These crystals attained their maximum size after four to six hours. The lime particles swelled up after eight to twelve hours and coloured yellow slowly. The newly-formed crystals, which were thought to be calcium eugenolate, fell to a yellowish porous mass after several days.

It was suspected that other constituents of cement might react in a similar manner with clove oil. It was found that calcium hydroxide rapidly became an intense yellow in contact with clove oil, but no new crystalline compounds were formed. In this way calcium oxide can be distinguished from calcium hydroxide, since a reaction similar to that of calcium oxide is shown only by strontium oxide, and in the case of calcium hydroxide only magnesium hydroxide shows a similar reaction with clove oil. Neither the other constituents of cement nor calcium salts, such as carbonate, chloride, sulphate, hydrated aluminates, or their double salts show any noticeable reaction with clove oil. In comparison with the well-known White's method, which depends on the formation of calcium phenolate, the clove oil reaction is much more useful because it allows a distinction to be made between calcium oxide and calcium hydroxide, which is not possible with White's method. In the case of White's method also the calcium phenolate crystallises throughout the whole field of view, while in the case of clove oil the crystallisation occurs only around the lime particles so that the individual particles stand out from the rest of the material.

The last section describes the glycolate method as worked out by Schläpfer and Esenwein. The preparation of the specimens is first dealt with as this is of great importance, since it has been shown that cements in the damp or set condition can take up considerable amounts of carbon dioxide during grinding. For instance, a set Portland cement which has been ground without any special precautions may show 7 per cent. free lime when the true value is about 0·5 per cent. The difference is caused by the absorption of carbon dioxide during grinding. Materials prepared for analysis by the glycolate method should be ground for a very short time until they pass a sieve with 100 meshes per sq. cm. and then 0·5 to 1 g. weighed out in a weighing bottle, at the same time keeping it out of contact with carbon dioxide as much as possible. The material is then placed in a small dry agate mortar together with about 5 c.c. ethylene glycol and carefully ground for about ten minutes. In this way the carbon dioxide is excluded and the glycol has a good opportunity of wetting the particles.

If the specimen is dry these precautions are not necessary. About 0·25 to 1 g. of the finely-ground material is weighed out, put into a round bottom-100 c.c. flask and mixed with 40 to 50 c.c. of neutral anhydrous ethylene glycol (sp. gr. 1·110) together with a pinch of quartz granules about 1 mm. size. The flask is shaken for thirty minutes in a water bath at 70 to 75 deg. C. The mixture is then titrated with alcoholic N/10 benzoic acid to a rose-brown coloration,

using phenolphthalein-α-naphtholphthalein as indicator. The mixture can also be filtered on a filter pump and titrated with N/10 hydrochloric acid. Three to four drops of indicator are used for the titration, the solutions being made up as follows: (1) 100 mg. phenolphthalein dissolved in 100 c.c. 98 per cent. ethyl alcohol, (2) 150 mg. α-naphtholphthalein dissolved in 100 c.c. 98 per cent. ethyl alcohol. The hydrochloric acid is preferably standardised with pure CaO. Since alkali oxides, hydroxides, carbonates, and bicarbonates are dissolved by ethylene glycol the lime in the ethylene glycol must be determined separately if these are expected to be present in large quantities. In this case the solution is evaporated, the ethylene glycol carefully driven off, and the lime precipitated as oxalate after taking up the residue with hydrochloric acid.

In analysing damp materials, besides the altered procedure described above, it should be noted that the titration must be stopped at the first change of the indicator from blue to pale rose-brown, because in the presence of large amounts of certain hydrated aluminates the indicator may turn blue again.

Rordam[4] replaced Schläpfer and Bukowski's indicator by another and altered the method so that a shaker was not necessary. Rordam's method, which is applicable to Portland cement clinker, is as follows: 1 g. of finely-ground clinker and a pinch of quartz sand are mixed with 30 c.c. of ethylene glycol and 15 c.c. of absolute methyl alcohol. The 200-c.c. flask is fitted with an air-cooled tube for reflux condensing and then held at boiling point for thirty minutes. The addition of methyl alcohol serves to hold the temperature between 82 and 84 deg. C. The vapour of the methyl alcohol also prevents the entrance of air and therefore the danger of rapid oxidation of the glycol. Finally the suspension is filtered, washed with alcohol, and bromthymol blue is put in as an indicator. N/10 hydrochloric acid is added in excess to give a yellow colour, and the excess acid is titrated back with N/10 sodium hydroxide until the colour changes to blue-green. In this way a sharper end-point can be obtained and tested repeatedly.

There is another method which has been described by Schläpfer and Esenwein[5] which deals with the problem as to whether the glycerate or glycolate method gives the correct result for the calcium hydroxide liberated in the hardening of cement or whether they decompose the hydration products and may give a deceptively high result for the liberated calcium hydroxide. In order to elucidate this problem a number of hydrated calcium aluminates, such as may be present in cement mortars, were tested individually for their behaviour in glycerine and glycol. The results showed that the glycolate method, including the modification by Schläpfer and Bukowski, could give acceptable results for set cements. However, compounds rich in water, especially the double salt Ettringite, $3CaO.Al_2O_3.3CaSO_4.31.5H_2O$ (cement bacillus), is definitely attacked. But since this plays an unimportant part in the composition of normal set Portland cements the error due to this source is small, especially when the glycerate method is used instead of the glycolate since the glycol attacks crystalline hydrated calcium aluminates more than does glycerine.

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[3] Mitteilung No. 109 from the *Eidgenössischen Materialprüfungsanstalt*, Zurich, pp. 19–32.
[4] *Rock Products*,, Aug. 1937, pp. 72–74.
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Design and Operation of Modern Lime Works.—XI *

By N. V. S. KNIBBS, D.Sc.

Temperature Measurement

If the temperature could be measured amongst the lime in the burning zone of an ordinary kiln it would be of the utmost value as an aid to kiln operation, but unfortunately measurement is possible only in static kilns, and even in them it is by no means easy to measure the temperature throughout the whole of the burning zone. In a vertical shaft kiln the flow of the lime prevents the introduction of a pyrometer into the burning zone. The best that can be done is either to insert a pyrometer in the refractory lining of the kiln or to obtain an instantaneous reading with a radiation pyrometer by sighting the lime through an opening with a radiation pyrometer. Neither of these methods gives a reading of the temperature in the interior of the burning zone. The first gives a reading which is below the temperature on the inside of the refractory lining by an amount which it is impossible to estimate closely. The second at best gives the temperature of the lime immediately in contact with the refractory lining, but in practice it is exceedingly difficult to avoid local cooling through the opening through which the pyrometer is sighted. In fact, under practical conditions temperature readings are likely to be more misleading than accurate, and the measurement of temperature in vertical shaft kilns is now seldom attempted. The temperature shown by a pyrometer inserted in the lining may be a useful guide in avoiding overheating the lining.

In static kilns of the ring type a portable pyrometer with a long stem to thrust through the arch into the burning zone is of considerable value.

In rotary kilns it is equally difficult to obtain a true reading of temperature, but the temperature of the lime leaving the kiln on its way to a separate cooler is a useful indication.

Of the other temperatures on a lime kiln, a knowledge of that of the exhaust gas leaving the kiln is useful and it should be taken immediately at the outlet of the kiln using a base metal thermo-couple with the indicator or recorder at any convenient position. It is not easy to obtain a correct temperature reading, even on a closed-top kiln, because of air leakage at the charging door. The outlet temperature is a guide to the efficiency of the kiln in that when the stone is dry the outlet temperature varies inversely as the efficiency, being low when the efficiency is high. Ordinarily, however, a kiln is charged intermittently, and the temperature changes in step with the charging (or with the discharging in kilns of the type shown in *Figs.* 7 to 10[9]) so that the average temperature—not any snap reading—is the guide to efficiency. The outlet temperature is greatly influenced by moisture in the stone charged, and therefore changes in the moisture content reduce its value as a guide to operation.

* Previous articles in this series appeared in our issues for January, February, March, April, May, August, September, October, November and December, 1937, and January and March, 1938.

[9] "Cement and Lime Manufacture," March, 1937, pp. 74 to 77.

In a kiln such as a rotary or a ring kiln, the temperature of the preheated air may be measured with a similar pyrometer and on a gas-fired kiln the temperature of the gas on its way to the kiln may be measured.

Gas Analysis.

A knowledge of the composition of the exhaust gases is of the greatest value. Carbon dioxide is a product of the dissociation of the stone, the amount liberated in the kiln being proportional to the amount of lime formed, and consequently the quantity in the exhaust indicates the amount of calcination that occurs. The carbon dioxide from the combustion of the fuel and, more particularly, the presence of excess air and incompletely burnt gas, introduce complications; nevertheless, from the analysis of the exhaust gases and a knowledge of the composition and calorific value of the fuel used the thermal efficiency of the kiln may be calculated.

The simplest instance is that of a mixed-feed kiln burning coke, with an exhaust free from oxygen and carbon monoxide. This ideal condition is never attained in practice, but efficient kilns may approximate fairly close to it. For each pound of carbon in the coke burnt 3.67 lb of carbon dioxide and 8,140 C.H.U.s (= 14,600 B.Th.U.s) are produced. The volume[10] equivalent to this weight of carbon dioxide is 29.9 cu. ft. and the volume of nitrogen in the air used for combustion is 113.2 cu. ft., so that the total volume of products of combustion is 143.1 cu. ft. In burning pure limestone the heat required per pound of carbon dioxide formed is 968 C.H.Us., or 119 C.H.Us. per cubic foot. If coke containing 1 lb. of carbon produces by calcination v cubic feet of carbon dioxide (using 119 v C.H.Us.) the total volume of carbon dioxide in the products of combustion is $29.9 + v$, and its percentage, a, is

$$a = \frac{100\,(29.9 + v)}{143.1 + v}$$

The thermal efficiency of the process of burning is the heat required for calcination divided by the heating value of the fuel, i.e., $\frac{119\,v}{8{,}140}$, or, as a percentage, $\frac{119\,v}{81.4}$

Expressing v in terms of a we have

$$v = \frac{(143.1\,a - 2{,}990)}{(100 - a)}$$

so that thermal efficiency of the kiln is

$$E = \frac{119\,(143.1a - 2{,}990)}{81.4\,(100 - a)}\ \%$$

$$= \frac{(209a - 4{,}370)}{(100 - a)}\ \% \qquad \ldots\ \ldots\ \ldots\ \ldots\ (1)$$

If the exhaust gases contain oxygen, due either to excess air passing through the kiln or to air drawn in at some point before that at which the gas is sampled for analysis, the excess air dilutes the gases and reduces the percentage of carbon dioxide. If both the carbon dioxide (a') and the oxygen (b) are measured the

[10] Measured at 0°C. and 760 mms.

extent of this dilution may be estimated and allowed for in the calculation. Each 20.9 parts of oxygen is equivalent to 100 parts of air, so that 1 per cent. of oxygen equals 4.79 per cent. of air, or b per cent. of oxygen equals 4.79 b per cent. of air. If the gases contain no free oxygen the percentage of carbon dioxide would therefore be

$$a = a' \times \frac{100}{(100 - 4.79b)}$$

Substituting this in equation (1) we have

$$E' = \frac{209\,(a' + b) - 4{,}370}{100 - 1.00a' - 4.8b}\ \% \qquad \ldots \quad \ldots \quad \ldots \quad (2)$$

$$\text{i.e. } E' = \frac{209\,(CO_2 + O_2) - 4{,}370}{100 - CO_2 - 4.8O_2}\ \%$$

Fig. 46 enables the efficiency to be read off directly from the gas analysis. If the expression of efficiency is required in terms of the ratio f of pure lime made to fuel burnt, and C is the calorific value of the fuel in C.H.Us. per lb., we have

$$E = \frac{f \times 760 \times 100}{C}$$

so that $f = \frac{EC}{76{,}000}$ or if C is in B.Th.Us., $f = \frac{EC}{136{,}800}$

Incomplete combustion, represented by carbon monoxide in the exhaust gases, vitiates the results unless it is determined by analysis and added to the carbon dioxide. The calculations are complicated by the presence of hydrogen in the combustible matter, either as hydrocarbon in coal or oil or as hydrocarbon and hydrogen in gas. Any hydrogen burns to water, using up oxygen, which must be allowed for in the calculations, and a different allowance is required for each different fuel, or a different set of curves. The author has obtained [11] the general expression for any fuel, and has drawn up curves for different types. For practical purposes, however, the complicated calculation of the true efficiency is unnecessary. The fluctuation of the carbon dioxide and oxygen show how the efficiency is varying, and by applying the values given by the curves in *Fig.* 46 a close approximation is obtained to the change of efficiency, which is sufficient for control purposes.

The exhaust gases may be analysed by any suitable form of gas analysis apparatus, such as the Orsat, but the value of such " snap " analyses is limited. An automatic gas analyser gives a chart of the composition, showing its fluctuation, and provides a record of kiln performance during the periods without expert supervision. The CO_2 recorder is obtainable in a number of different forms, in most of which the carbon dioxide is absorbed in a caustic solution and the decrease in volume automatically measured and recorded. The usual instruments are made for flue gas analysis, where the maximum CO_2 is 21 per cent., and their scale is insufficient for lime kiln gases, for which a special instrument graduated up to 40 per cent. is required. In another form the differential pressure across a porous diaphragm, with a CO_2 absorbent on one side, provides a measure of

[11] Knibbs—Lime and Magnesia, London, 1924, p. 177 *et. seq.*

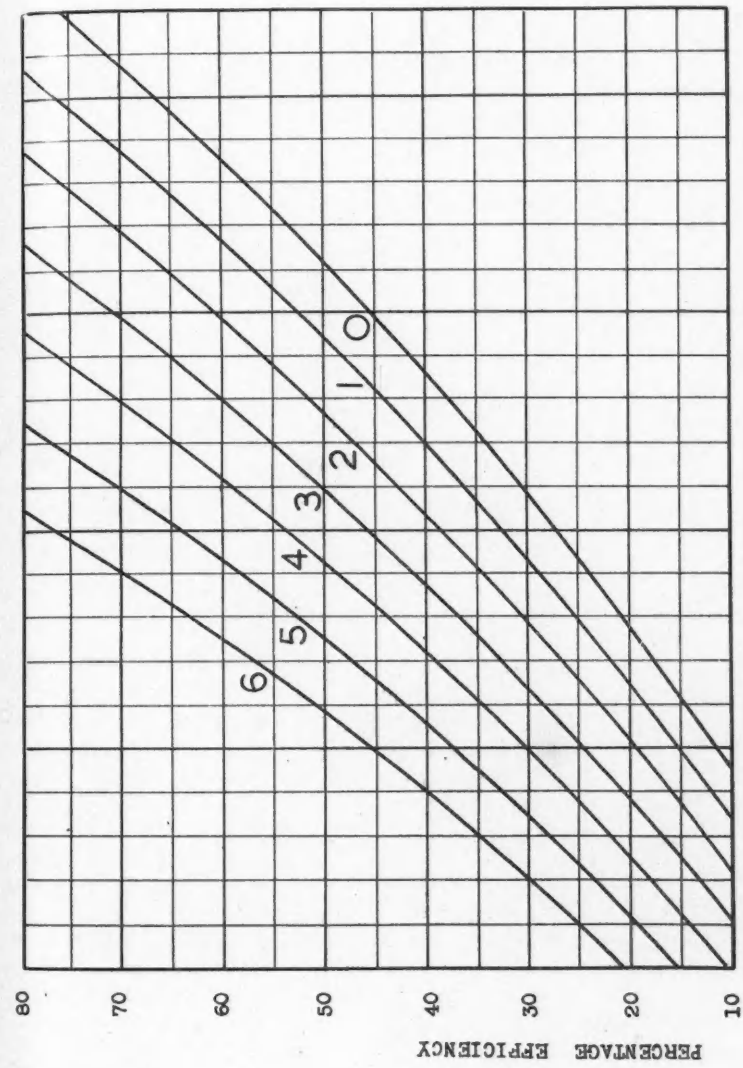

Fig. 46.—Kiln Efficiency for different Exhaust Gas Compositions.
The figures against the Curves represent the percentage of Oxygen in the Exhaust Gases.

the percentage, and in still another form the change of thermal conductivity of the gas, measured electrically, is used to indicate and record the CO_2 content. The electrical (thermal conductivity) method has the merit of not ordinarily requiring an absorbent (which has to be changed when exhausted), but on a producer-gas-fired kiln the incomplete combustion of the gas will vitiate the results of this absorbent-free type. In this method the instrument measures the decrease of thermal conductivity due to increase of CO_2 content, which decrease is due to the lower thermal conductivity of carbon dioxide compared with air (against which it is measured). Some gases, in particular hydrogen, have a higher conductivity than air and the increase of conductivity effected by hydrogen is many times greater than the decrease effected by the same percentage of carbon dioxide. Consequently a very small percentage of unburnt hydrogen from the gases will give a false low reading of carbon dioxide. To overcome this in the electrical instrument (which is the most convenient in that the indicator or recorder or both may be placed anywhere convenient and distant from the analyser) an absorbent is used and the conductivity of the gas compared before and after absorption, the difference giving a true measure of CO_2.

These instruments which measure only carbon dioxide are of value in assessing kiln performance only if the leakage of air into the exhaust gases is small and reasonably constant in amount. They are therefore useful in enclosed-top kilns with tight charging doors, and especially in mixed-feed kilns burning coke. Forced-draught kilns are less likely to draw in diluting air than exhausted kilns. On most kilns, and especially on gas-fired kilns, an analyser which measures both the carbon dioxide and the oxygen is of much greater value, and there is an electrical instrument for this purpose, which will record the percentage of CO_2 and oxygen on one chart. It is also possible to measure the carbon monoxide together with the carbon dioxide and oxygen on an electrical analyser, and these three quantities give a complete picture of the kiln performance.

When carbon burns to carbon dioxide it liberates much more heat than when only carbon monoxide is formed, the heat evolved in monoxide formation being only 30 per cent. of that of dioxide formation. In a kiln of good efficiency each 1 per cent. of carbon monoxide in the exhaust gases represents about 6 per cent. of the total carbon burnt, and therefore for each 1 per cent. CO more than 4 per cent. of the total heating value of the fuel is wasted.

Gas-flow Measurement.

In the great majority of kilns a water-gauge manometer is the only indicator of draught that is used, and, as already shown, this cannot measure the actual flow, that is, the weight of gases passing in unit time. For a true measurement some kind of flow meter is necessary. There are several available, but only the simplest and least costly need be considered here. The simplest flow meter consists of an orifice plate and a differential pressure gauge. The orifice plate, which is simply a circular metal plate with a round or other shape hole in the middle, is placed at a joint in a straight length of pipe carrying the gas to be measured. The hole should preferably have sharp edges. On each side of the

orifice plate, and at definite distances from it, connections are made to the differential gauge so that the difference of pressure on the two sides is measured. The drop of pressure at the orifice is proportional to the square of the rate of flow, and for any particular orifice plate the differential gauge may be calibrated in rate of flow. Better, but more costly than an orifice, is a Venturi tube, whilst another and cheaper instrument is the Pitot tube. In all these instruments the differential pressure registered is a function of the square of the rate of flow, and consequently low rates of flow cannot be read as accurately as high rates. To provide a more evenly spaced scale differential gauges have been designed in which the pressure scale closes up as the pressure is increased.

In all such instruments the difference in pressure depends on the weight of gas passing in unit time and also on the composition and temperature of the gas. Accuracy also depends upon the cleanliness of the orifice (or other device) and of the flue upstream and downstream. The exhaust gases from a lime kiln contain smoke and dust which tend to deposit on the vital parts and affect the results but, more important, the varying temperature and composition of the exhaust gases make it impossible to graduate an instrument to indicate directly the flow. Each reading must be corrected for temperature and composition. A flow meter on the exhaust gas flue is therefore of little value on a lime kiln. On the other hand, a meter for the air used is reasonably accurate, because of the comparatively narrow variation of temperature and the cleanliness of the air. Forced-draught mixed-feed kilns are therefore well adapted to flow measurement.

Gas-fired kilns are nearly always exhausted. The air blown to the producers can be measured and this provides a good guide to the volume of gas, but the air for combustion cannot ordinarily be measured. In kilns provided with waste-heat boilers the temperature of the gases leaving the boiler varies much less than at the point where they leave the kiln, and consequently they are better adapted for measurement. However, the analysis of the exhaust gases provides much better control of the operation of the kiln than measurement of the flow, and an automatic exhaust-gas analyser, preferably accompanied by a flow meter on the gas (if it is clean gas) or on the air supplied to the producer, provides all the data necessary for the efficient control and operation of the kiln.

How Lime Deteriorates in Burning.

If a piece of limestone is heated in an electric furnace at, say, 950 deg. C. until it is completely calcined, the lime obtained is very different from the lime made in a commercial kiln. The reasons for the difference will now be discussed. There are six main causes of deterioration of lime in burning, namely, overburning, recarbonation, underburning, absorption of sulphur, contamination by ashes, clay, etc., and moisture absorption. For most purposes the lime made as mentioned, that is by exact burning at low temperature without exposure to contaminating influences, would be unsuitable for ordinary commercial use. It would be so highly reactive, that it would absorb too much moisture in storage and transit, and also it would be difficult to slake satisfactorily to a putty. Nevertheless the influences which are responsible for changing such highly-reactive

lime into a good commercial lime, will, if prolonged, bring about a further change causing deterioration of the lime for most purposes.

Overburning.—The overburning of lime is due to its being exposed to too high a temperature for too long a period. There are no exact data on the effect of temperature and time, and the little that is known has already been given[12]. In actual kilns overburning may be due to several causes. If the kiln temperature is too high throughout, the whole of the output will be overburnt, but this seldom happens with a pure lime because it will withstand a higher temperature than any refractory kiln lining at present available. Uneven heating of the kiln, by uneven fuel distribution in a mixed-feed kiln or of distribution or penetration in a gas-fired kiln, may produce lime overburnt in parts, and this is a common occurrence in most kilns. Such overburnt lime is ordinarily separated by sorting. Another cause of overburning is the uneven flow of limestone through the kiln, causing some portions of the lime to remain too long in the hot zone, with consequent overburning. Since pure lime will withstand a very much higher temperature than magnesian or hydraulic lime, the temperature margin between the minimum burning temperature and the temperature at which overburning takes place is much wider with the pure lime. Consequently the chances of overburning are much less and less care is necessary in operating kilns producing pure lime.

Recarbonation.—Recarbonation is the reconversion of lime to carbonate by absorption of carbon dioxide gas in the cooling zone of the kiln. It generally occurs through a down-draught in the kiln, but may also occur in a mixed-feed kiln through the descent of burning carbon into the cooling zone, and in a gas-fired kiln through absorption of carbon dioxide from the gas itself. The influence of recarbonation on the properties of the lime is considerable, and resembles in many ways the effect of overburning with which it is often confused. Recarbonation is prevented by proper arrangement of draught, and, in mixed-feed kilns, by distributing the fuel so that its combustion is even.[13].

Underburning.—Lime that is generally considered underburnt is that in which there is a core of unburnt limestone in the centre of the lump of lime, but it is possible to have lime that is " underburnt " for some specific purpose but which is nevertheless completely calcined.

Underburning, leaving a core in the lime, is due to an insufficient period of heating at the temperature of the burning zone for the particular size of the stone being burnt. Ordinarily the underburnt lumps are the largest, but sometimes quite small pieces pass through underburnt due to their being masked by a large piece and consequently receiving insufficient heat. Underburning is also a common fault in gas-fired and oil-fired kilns fitted with side burners only, and in furnace-fired kilns. When such kilns are operated so that no underburnt lime is drawn there is almost always some lime that is overburnt. In a mixed-feed kiln the proper distribution of the fuel and the even sizing of the stone minimise the chances of underburning, and in a gas-fired kiln, apart from correct design,

[12] " Cement and Lime Manufacture," July, 1937, p. 201.

the even sizing of the stone and the proper regulation of gas and air do the same thing.

As already mentioned, lime that is burnt free from core may still be underburnt from the point of view of its use. A very lightly burnt lime not only travels badly, especially in hot and humid weather, but it is also difficult to slake without " burning "[14]. However, it is seldom that conditions of burning are so good as to underburn lime in this way without leaving excessive core.

Sulphur in Lime.—One effect of sulphur in lime has already been discussed.[15] The quantity that can be tolerated varies widely, and for ordinary building purposes it is seldom that the sulphur content of the lime causes comment. For chemical purposes the amount of sulphur that may be present depends on the use and no fixed limits can be set. Sulphur contamination of the lime is prevented by using a fuel low in or free from sulphur. If a low-sulphur coal is not obtainable the gasification of the coal and the subsequent purification of the gas will eliminate the sulphur, but this is seldom commercially feasible. The addition of a small amount of lime to the producer will reduce the sulphur content of the gas, but the degree of sulphur reduction is doubtful.

Ashes, Clay, etc.—Contamination of the lime by ashes is avoided by using an ash-free fuel, that is to say by using oil, producer gas, or other gas. In a mixed-feed kiln it is minimised by charging in layers of substantial thickness or, more effectively, by using a fuel with an ash of high fusing point and operating the kiln at relatively low temperature. The ash is then nearly completely separable from the lime by sorting or screening. Clay or other impurity introduced into the kiln on the limestone is bound to contaminate the lime in some degree, and the charging of such impure stone should be avoided ; if it is unavoidable a low burning temperature enables most of the impurity to be eliminated by screening from the lime drawn from the kiln.

Absorbed Moisture.—In all modern kilns the air for combustion is drawn through the lime in the cooling zone. All moisture contained in that air is absorbed by the lime, reducing its reactivity and its " available lime " content. The amount of water that is absorbed depends upon the humidity of the air and the volume of air used per unit of lime produced. It is evident that the higher the thermal efficiency of the kiln the less will be the air used, and therefore the less the moisture absorbed by the lime In a mixed-feed kiln burning coke, with a lime-to-fuel ratio of 5 to 1 the amount of air used is about 25 cu. ft. per lb. of lime. In summer weather, in England, the maximum humidity experienced may be of the order of 0.12 lb. of water per 100 cu. ft., that is, 0.03 lb. per lb. of lime, or 3 per cent. Such high humidity is exceedingly rare in England, and ordinarily it is very much less. In tropical countries the absorption may be considerably greater.

The effect of this absorbed moisture on the properties of the lime is much greater than the percentage figures would suggest,[16] and it must also be realised that there is always further absorption from the atmosphere after the lime is withdrawn from the kiln.

Auxiliary Agents in Lime Burning.

In furnace-fired kilns it was in the past a frequent practice to blow steam into the kiln with the flame, it being supposed that steam assisted the calcination reaction and increased the production of lime and the efficiency of the fuel. By diluting the gases and thereby reducing the partial pressure of carbon dioxide this steam would slightly reduce the equilibrium pressure, but its effect in reducing the flame temperature would more than balance any good this might do and the result would be unfavourable. There remains the possibility of catalytic action, and it is known that the attainment of equilibrium between carbon dioxide and lime is promoted by a trace of moisture.[17] On the other hand, it has been shown[18] that calcium carbonate dissociates normally even after intensive drying. It is unlikely that under practical conditions of lime burning a substance added at that point could influence more than the outside of the lumps of lime, and as it is the interior of the lumps which control efficiency and rate of burning, steam is unlikely to have an appreciable effect.

Another alleged aid to lime burning is salt, which in some places is added to mixed-feed kilns with the fuel. This, too, is an old practice, especially in France, and its persistence over a long period is prima facie evidence of its value. It has been investigated by Duchez and de Joux,[19] the former of whom confirmed that the addition of 0.1 per cent. of sodium chloride to the coal in several kilns resulted in a saving of 15 per cent. to 25 per cent. of the fuel, whilst the latter found hydrochloric acid and phosgene in the kiln gases at the burning zone. Duchez found that there was abnormal fusion of the lining in the kilns using salt, which he attributed to the hotter fire. Here, again, it is difficult to see how salt added to the coal can influence directly the calcination of the interior of pieces of limestone. The effect, if it is a real one, is probably due to a modification of the reactivity of the fuel itself, resulting in its combustion in a manner more suited to lime burning. The abnormal fusion of the lining may be due to a hotter fire, but it may alternatively be due to the fluxing of the firebrick by the salt acting as a glaze.

(*To be continued.*)

REFERENCES.

[13] See also " Cement and Lime Manufacture," Feb., 1937, p. 53.
[14] " Cement and Lime Manufacture," July, 1937, p. 204.
[15] *Ibid.*, p. 200.
[16] See " Cement and Lime Manufacture," July, 1937, p. 202.
[17] Mitchell.—*J. Chem. Soc.*, 123, 1055 (1923); Andrussov.—*Z., physik. Chem.* 116,18 (1925); Jolibois and Bouvier—*Compt. rend*, 172, 1182 (1921).
[18] Sossman, Hostetter and Merwin.—*J. Wash. Acad.* Sc. 5, 563 (1915).
[19] Duchez—*Rev. Mat. const. trav. publics.* 1930, 8; de Joux—*ibid*, 1933, 92.